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Title:	High efficiency environmental sampling with UV-cured peelable coatings (aka NuGoo project)
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High efficiency environmental sampling with UV-cured peelable coatings
(aka NuGoo project)

Vlad Henzl, Ann Junghans and Rollin Lakis

[1)] *Safeguards Science and Technology (NEN-1), Nuclear Engineering and Nonproliferation Division*

CA Related Project (FY13-17)

- WG1 – compiled list of proliferation indicators based on Physical Model and Wacker Report **FY13**
- WG2 – considered various detection methods and associated COTS handheld tools for various proliferation indicators **FY13**
- WG3 – “qualitative” lab/field test of XRF, Raman and FTIR against many proliferation indicators **FY14**
- LANL - Quantitatively evaluate the performance of hand-held instruments under conditions like during IAEA CA, determine trace sensitivity for U and Th **FY15**
- LANL (II) – Evaluate Hyper Spectral Imaging Technology for use during Complementary Access **FY16/17**
- LANL (III) – Environmental sampling with UV curable peelable coatings (aka NuGoo project) **FY17**

Environmental sampling by IAEA (not only) during CA

Graded approach sample analysis:

1) Low background γ-spectroscopy (U, Pu, fission and activation products)
2) XRF spectrometry to detect/locate uranium particulates
3) Optional α and β counting to detect actinides or β emitting isotopes (^{3}H, ^{90}Sr, ^{99m}Tc, etc.)
4) Subsamples distributed to NWAL, selected ones destructively assayed using inductively coupled plasma mass spectrometer

Pro's and Con's of cotton based ES:

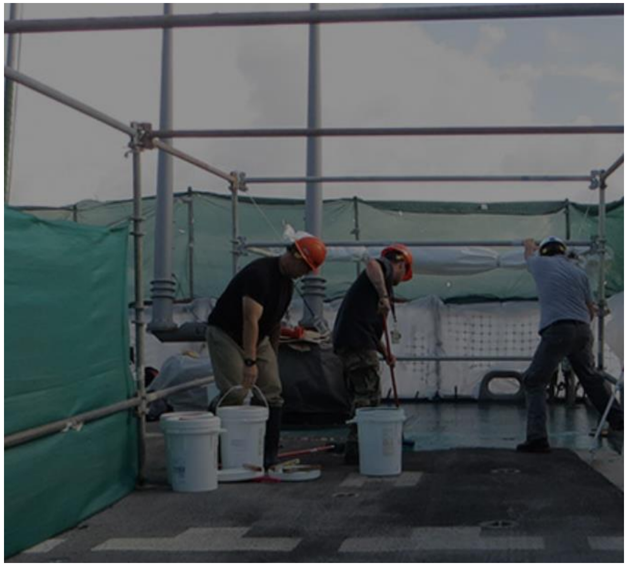
+ High sensitivity ~1-10 ng of U, 1-5 fg of Pu

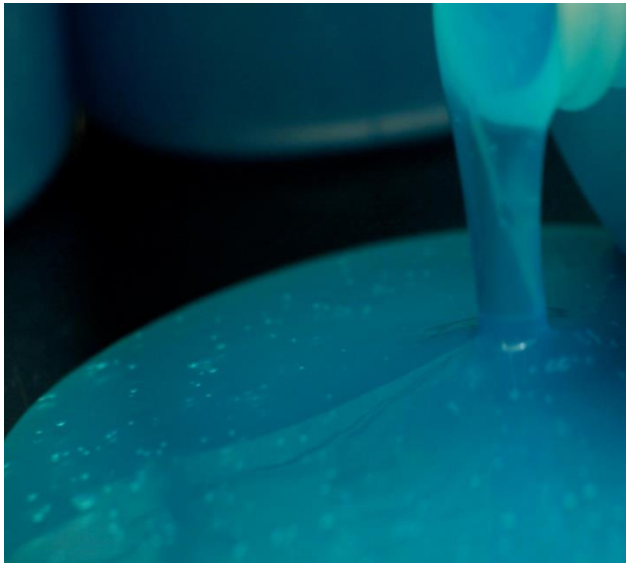
+ Precise isotopic characterization

- High cost (~k$/sample), feedback delayed by weeks/months
- Low laboratory throughput (100-200 samples/year) => ***1 ES kit per inspection***
- Low sampling efficiency, analyte not bound in swipe matrix
- Prone to operator's error, unsuitable for certain surfaces (cracks, pores, etc.)

Decontamination gels

- Well developed commercial product
- Used routinely for decontamination of decommissioned facilities or contaminated instruments, cleaning up spills etc.
- Polymer based hydrogel with chelant to attract heavy metals (U, Pu, etc.)
- Applied to surface, dries & “rubberizes” overnight, easily peeled-off
- ***In FY15 we used small decon gel amounts for environmental sampling***

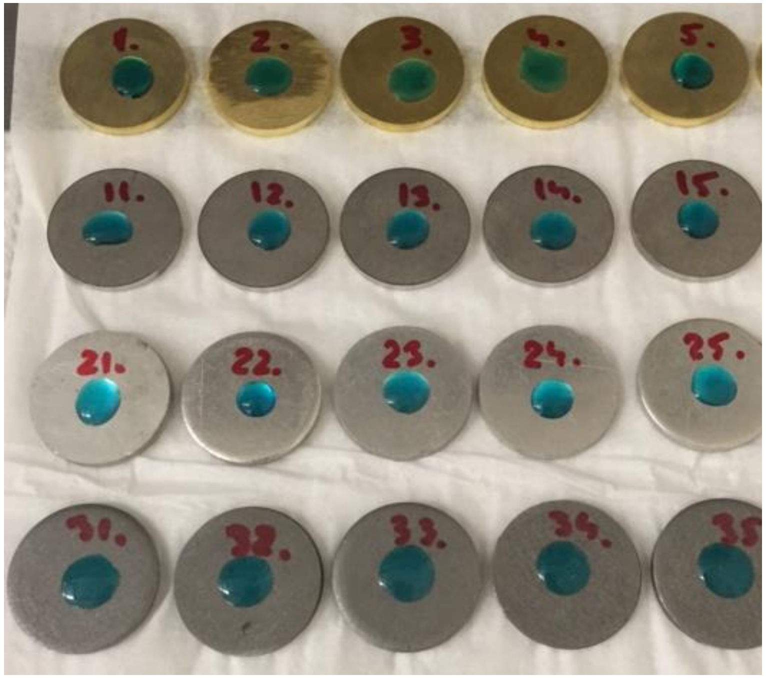


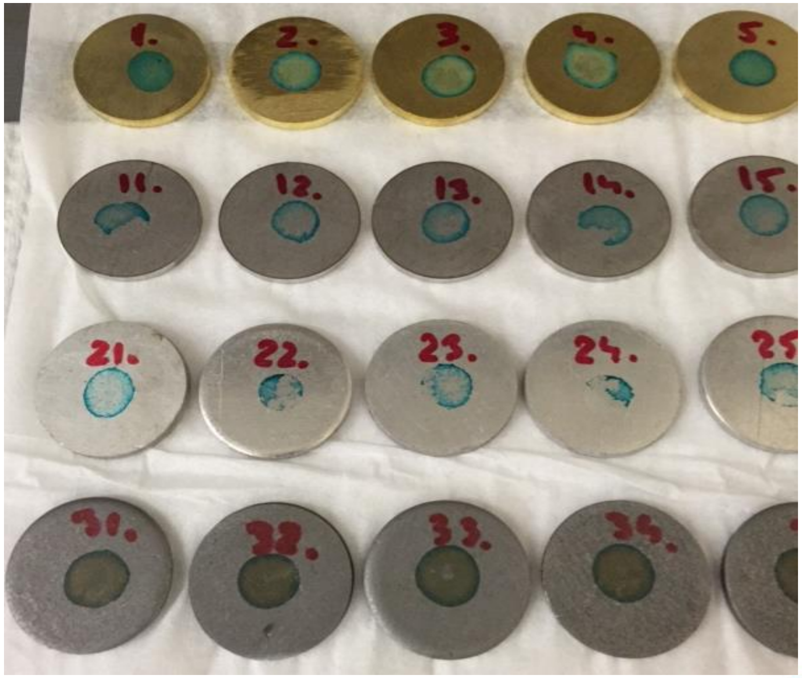


Source: decongel.com

Cotton swipes vs. decon gel (FY15)

- 10-20 μg of U applied to various industrial surfaces (*aluminum, brass, steel, stainless steel, wood, concrete, glass, lead*)
- Surfaces swiped with cotton and cleaned with decon gel
- Removal rates and residues analysed using XRF spectrometer





Contamination removal study

TexWipes (cotton cloth)

material	Removed from sample [%]	Captured on swipe [%]
Aluminum (Al3003)	15	10
Brass (C26000)	10	10
Steel	7	4
Stainless Steel (SS304)	53	35
Lead	21	4
Concrete	51	8
Glass	20	10

~ 10 min procedure
- Low removal efficiency
- Can swipe large area
- Not suitable for porous material (e.g. wood)
- Analyte can fall off the swipe

Dried and peeled off decontamination gel

material	Removed from sample [%]	Captured on swipe [%]
Aluminum (Al3003)	47	47
Brass (C26000)	42	42
Steel	62	62
Stainless Steel (SS304)	91	91
Lead	100	80
Concrete	n/a	n/a
Glass	85	54

~ 6 hr drying time
- High removal efficiency
- Applied to limited area
- Seeps into cracks
- All removed analyte embedded in matrix

The origins of the NuGoo

- Decon gel based sampling very effective, but ***drying too slow***

  => How can we speed up the drying ?

!!! Let's make decon gel UV curable, and "dry" it within seconds !!!

- LANL program office provided program development funding for proof of principle
- We focused on three critical areas of the new concept

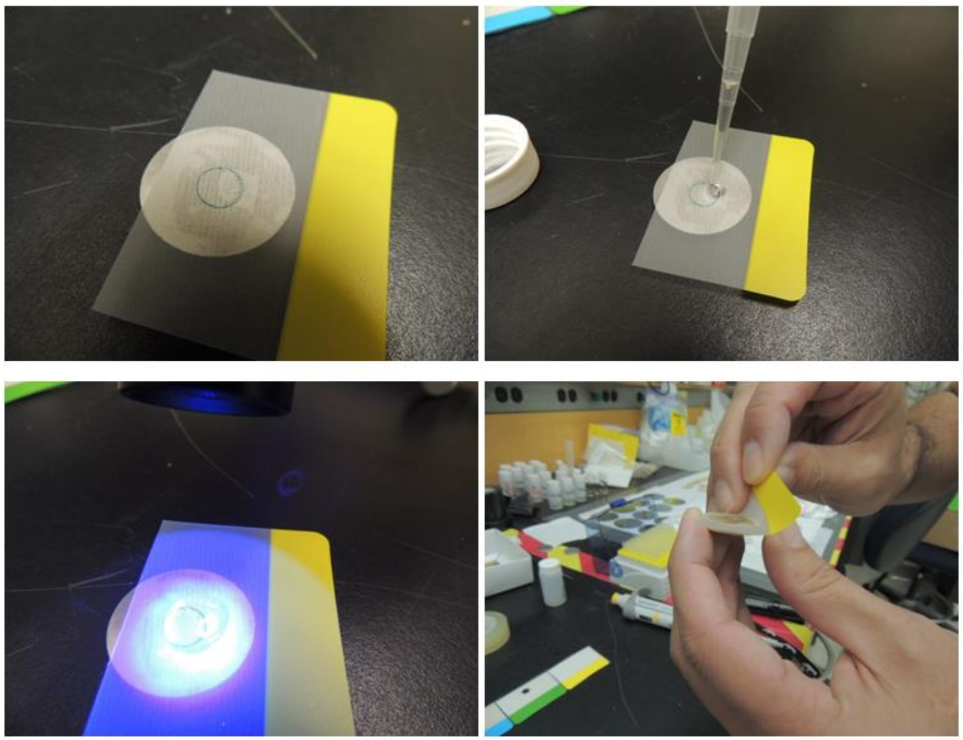
- Commercial UV curable peelable coatings available (typically for masking)
  - => how much can they remove ?
  - => are they suitable for porous surfaces ?
- Industrial UV lamps not practical
  - => can pocket LED UV flash lamps work ?
- How to remove the cured polymer ?
  - => … without using your fingernails …

NuGoo – proof of concept

- Mixture of two commercial products and ~ 25% of ethanol
- 3W 365nm LED UV flashlamp
- Perforated plastic stencil

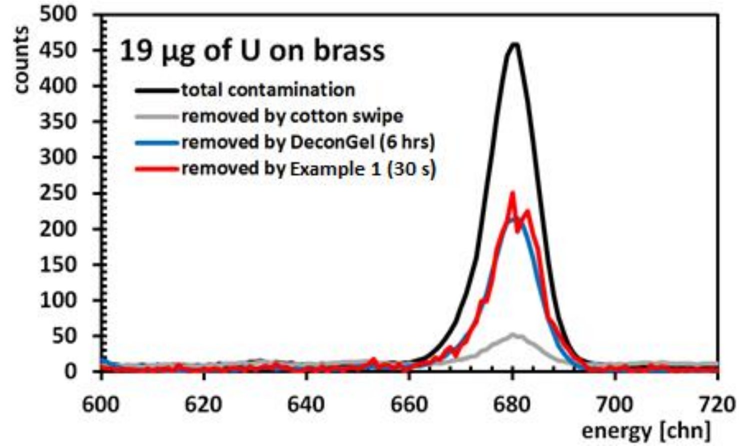
Procedure:

1. Apply stencil to area, press
2. Apply <1 ml of UV curable gel



3. Apply UV light for ~30 s
4. Detach stencil

Initial results indicate similar results as with regular decon gel



NuGoo – FY17 project ($250K)

- Formulate own polymer mixture(s)
- Test curability, peelability, and removal rates of dried uranyl residues as function of:

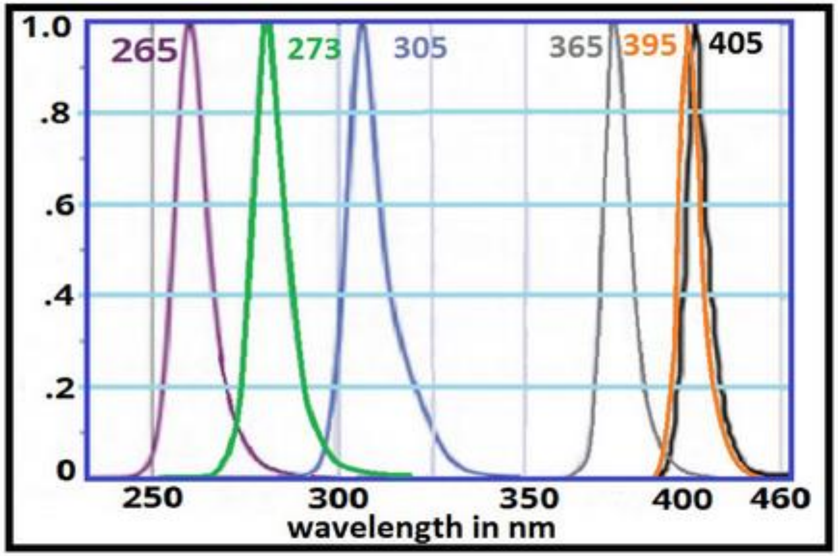
  => polymer, LED lamp, additive, surface, stencil geometry

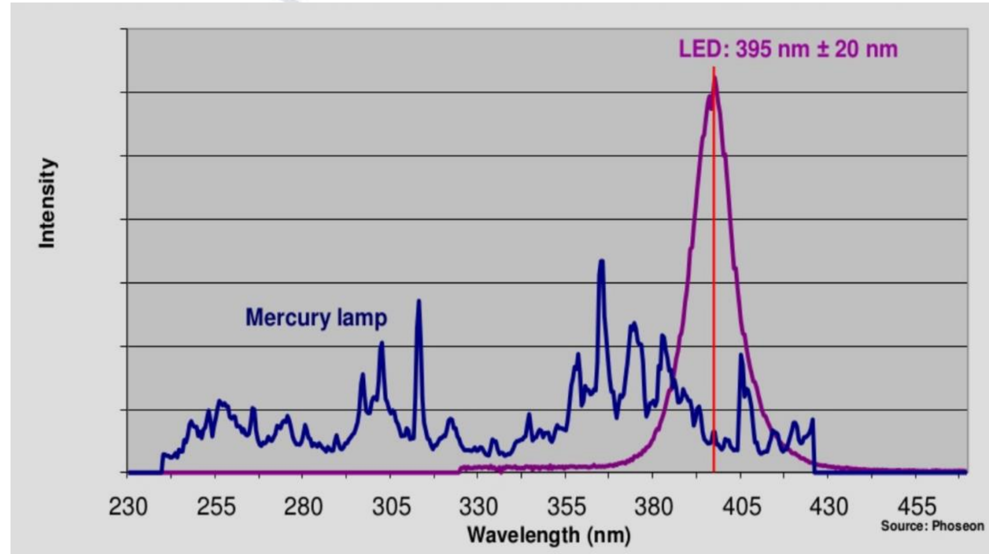
- Quantitative evaluation by XRF

Criteria of success:

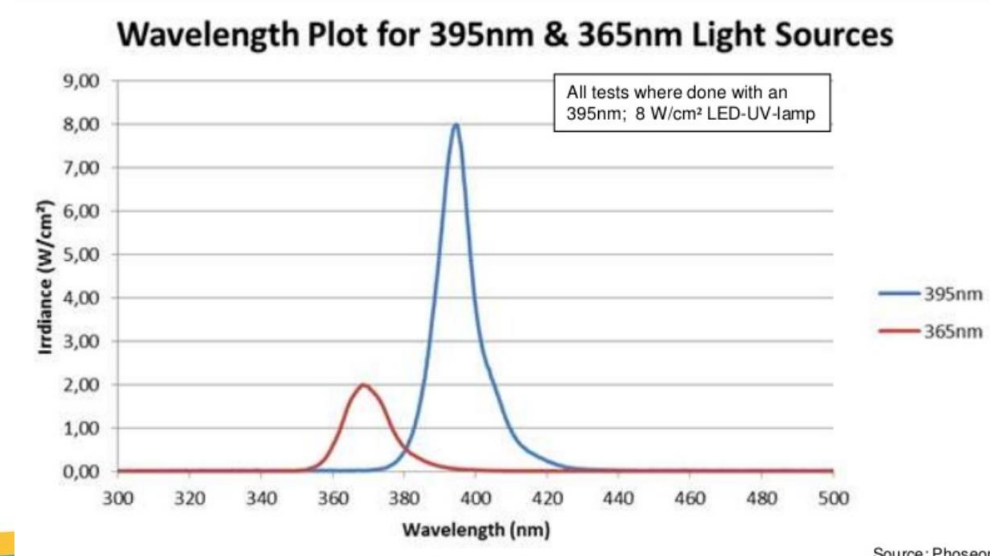
1) Removal rates (>50%)
2) Cured within 30s with pocket UV LED flashlamp
3) Complete peelability without leaving residue from range of surfaces
4) Uncured polymer nonhazardous (i.e. safe to handle)
5) Matrix (polymer+stencil) clear of interfering contaminants (e.g. heavy metal traces)

LED lamp
– which one works and why





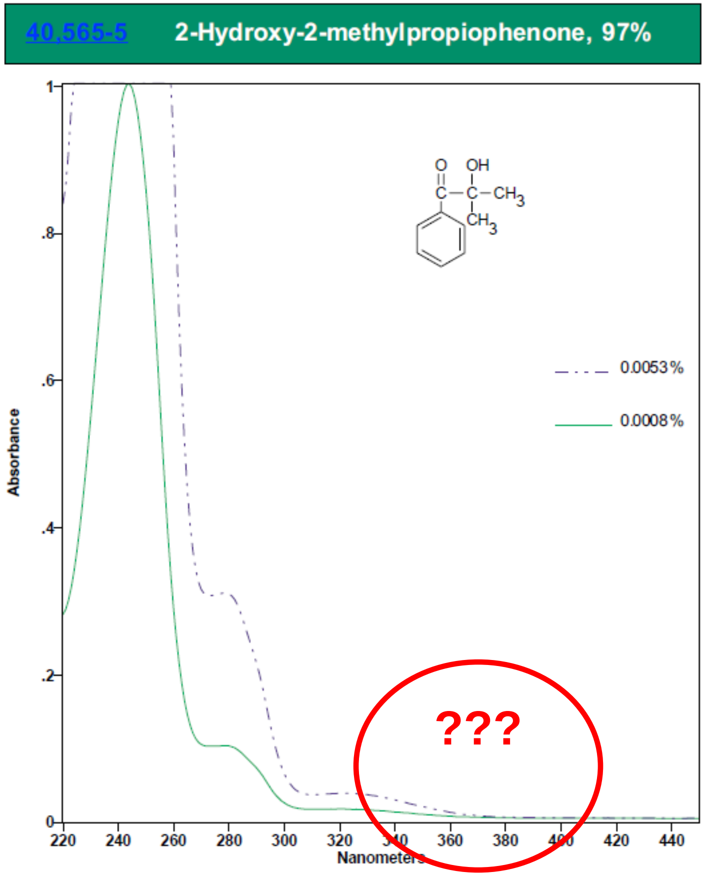
LED Type	Wavelength (nm)	Output (mW)
UVC-LED	260-265	0.22-0.5
UVC-LED	270-280	1-1.6
UVC-LED	305-315	1
UVA-LED	365-370	30-40
UVA-LED	361-371	135
UVA-LED	390-400	320
UVA-LED	387-392	680
UV-VIS LED	400-410	557



Selecting photoinitiator

- Has to absorb in emission range of LED lamp
- 49 common photoinitiator at Sigma Aldrich
  - *- Benzoin ethers*
  - *- Benzil ketans*
  - *- a-Dialkoxyacetonephenones*
  - *- a-Hydroxyalkyl phenones*
  - *- a-Aminoalkyl phenones*
  - *- Acylphosphine oxides*
  - *- Benzophenones/amines*
  - *- Thioxanthones/amines*
  - *- Titanocenes*

- Only 5 deemed suitable for curing with 365/395nm LED lamp (one Cat 1 carcinogen)
- Selected four for trials:
  - ***4-(dimethylamino) benzophenone***
  - ***Thioxanthene-9-one***
  - ***4,4'-bis(diethylamino) benzophenone***
  - ***Phenyl bis (2, 4, 6-trimethylbenzoyl phosphine oxide)***



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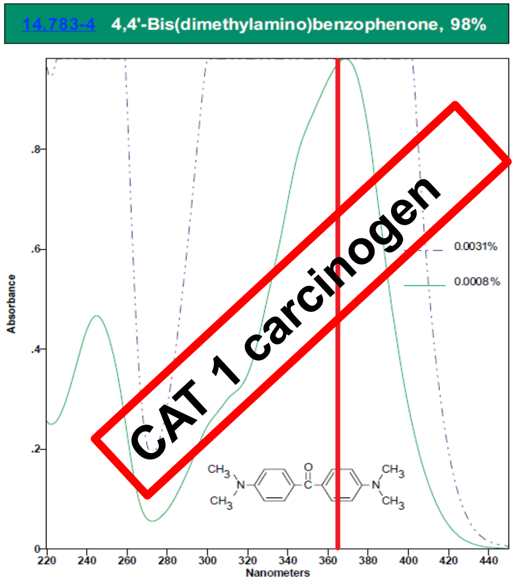

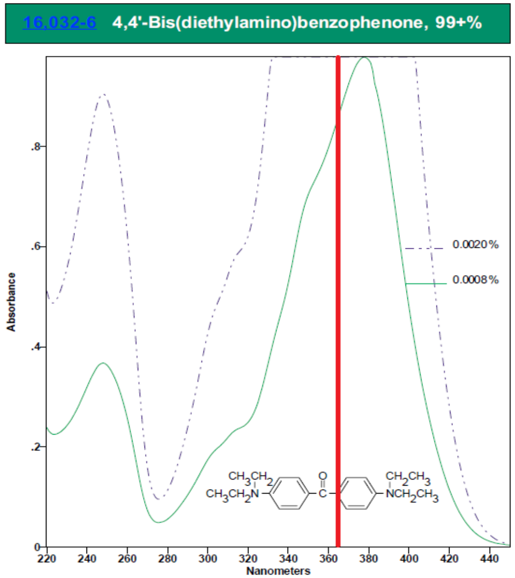

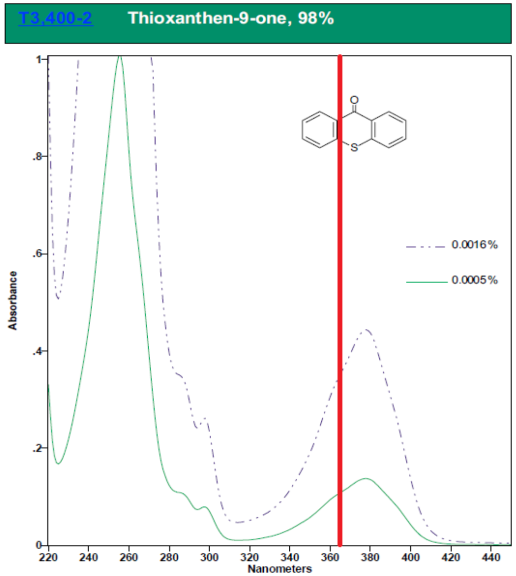

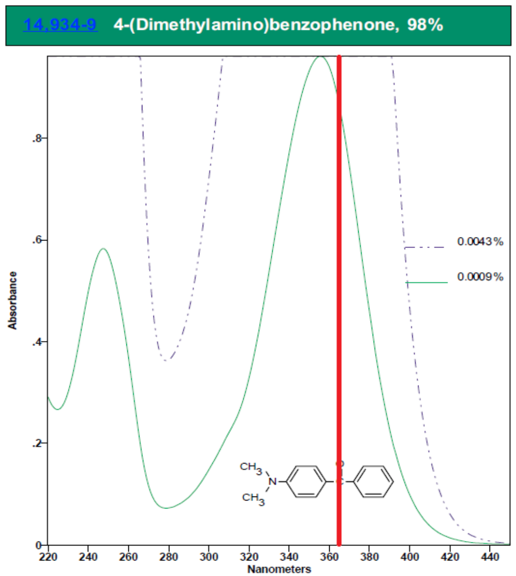

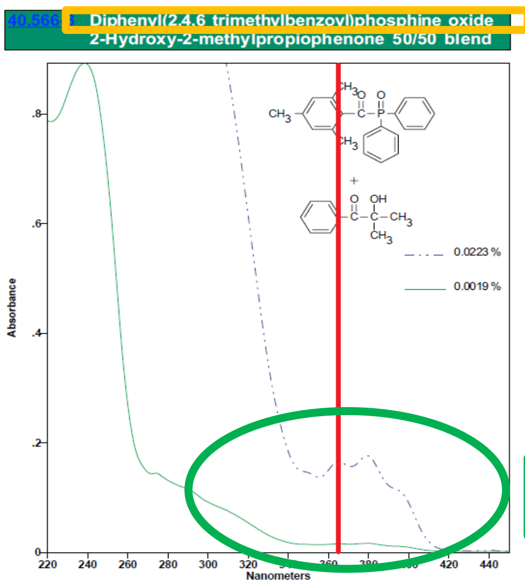

BEST !!!

Monomers and oligomers

- Endless choices
- Focus on acrylates, urethanes, vinyls
- Main criterion => ***NONHAZARDOUS*** *(& affordable)*

- Originally selected for trials:

16 monomers

- 1,4-butanediol
- 1,5-pentanediol
- 2-[[(butylamino)carbonyl]oxy]ethyl acrylate
- 2-hydroxy-2-methyl propiophenone
- 2-hydroxy-3-phenoxypropyl acrylate
- Butyl acrylate
- Di(ethylene glycol) 2-ethylhexyl ether acrylate
- Di(ethylene glycol) ethyl ether acrylate
- Isobornyl acrylate
- Poly(propylene glycol) acrylate
- Poly(tetrahydrofuran)
- Tetrahydro furfuryl acrylate
- Tri (ethylene glycol) divinyl ether
- Trimethylol propane ethyloxylate triacrylate
- Trimethylopropane triacrylate
- Tri(propylene glycol) diacrylate

4 oligomers

- Soy bean oil epoxidized acrylates
- 2-carboxyethyl acrylate oligomers
- Polytetrahydrofuran
- Polivinyl pyrolidone

2 commercial coatings

- UV 733
- Tangent02019

Results *(they are goo'ed !!!)*

- ~ 200+ curable mixtures (curing times 5-30 s)
- 500+ blanks (wood + steel) used
- 2700+ XRF measurements, 50+ calibrations
- 15+ Goos fully evaluated for removal rates
- *Adhesion ranges from "non-removable" to " jumps-off by itself"*
- *Physical properties "credit card goo" to "solid as rock"*
- *Peelability "poor" to "great"*
- *Removal rates*
  - 3% to 75% on steel
  - 3% to 26% on wood

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Results *(they are goo'ed !!!)*

Pure commercial coatings:

Coating	steel	Wood
DeconGel	**92%**	**58%**
UV733	51%	8%
Tangent 02019	43%	8%

Customized and in-house developed coatings:

Coating	steel	Wood
UV733+Tangent 02019 (25:75)	70%	20%
UV733+Tangent 02019 (50:50)	61%	7%
UV733+Tangent 02019 (75:25)	67%	12%
UV733 + max ethanol (30%)	72%	n/a
Tangent 02019 + max ethanol (30%)	44%	13%
M5+P4	35%	5%
Sendin-2b2	**75%**	19%
Sendin-2b2 + SodiumCitrate	40%	**25%**
Sendin-2b2 + EDTA		3%
Sendin-2b2 + Tiron		6%
Sendin-2b2 + Ascorbic Acid		3%
Sendin-Ur	36%	**25%**
Sendin-Ur + Ascorbic Acid		17%
Sendin-Ur + Tiron		16%
Sendin-Ur + SodiumCitrate	41%	12%

SuiteGoo
– five flavors of Goo for CBRNE

Los Alamos NATIONAL LABORATORY EST.1943

NuGoo - UV coating + chelant/solvent + XRF/NWAL => SNM traces

BioGoo - UV coating + nonionic detergents + bead beating => DNA profile

NanoGoo - UV coating + nanoparticles + infra-red Raman
=> chemical traces analysis (e.g. explosives)

RaGoo - UV coating + fluorescing agents + liquid scintilator
=> very low decay counting (e.g. ^{212}Po)

GlowGoo - UV coating + sensitizer + optical spectroscopy
=> trace detection of actinides

Patentable Invention

HIGH EFFICIENCY ENVIRONMENTAL SAMPLING WITH RAPIDLY CURED PEELABLE COATINGS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to and the benefit of U.S. Provisional Application No. 62/408589, filed October 14, 2016 and titled "HIGH EFFICIENCY ENVIRONMENTAL SAMPLING WITH RAPIDLY CURED PEELABLE COATINGS", the entire content of which is incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] The United States government has certain rights in this invention pursuant to Contract No. DE-AC52-06NA25396 between the United States Department of Energy and Los Alamos National Security, LLC for the operation of Los Alamos National Laboratory.

BACKGROUND

[0003] Environmental sampling and forensic evidence collection is often performed by swiping a surface suspected to contain an analyte of interest with cotton swipes or swabs. The collection efficiency of such swipes or swabs is typically low (about 10% to less than 1% of the total environmental presence of the analyte), and strongly depends on the chemical and physical properties of the analyte as well as the type of surface from which the sample is collected. For example, the collection efficiency by cotton swipes of analytes embedded in surfaces of porous materials such as wood, concrete, or fabric is substantially or practically zero. Furthermore, the analyte collected by dry cotton swipe or swab is susceptible to being literally shaken off the loose cotton matrix during transport, resulting in further loss (typically about 10 percent or more of the total collected amount) of the analyte during transport or storage. Additionally, environmental and operator variations in swiping technique result in data that may be difficult to quantitatively interpret and reproduce.

[0004] Therefore, existing cotton swipe and swab based sample collection techniques and materials are often unsatisfactory for the accurate and sensitive detection of trace amounts of chemical, biological, radiological, nuclear, or explosive (CBRNE) material and are generally not suitable as means of preserving the collected sample as forensic evidence.

SUMMARY

[0005] According to embodiments of the present disclosure, a kit for collecting an analyte from a sampling surface includes a rapidly curable liquid gel and a portable device to enable rapid curing. The rapidly curable liquid gel may include a polymer precursor mixture including a monomer and/or an oligomer; and an additive selected to enhance extraction of the analyte from the sampling surface. In some embodiments, the kit may further include a stencil including openings through which a portion of the rapidly curable liquid gel can pass to directly contact the sampling surface.

[0006] In some embodiments, the rapidly curable liquid gel may further include a cure activator component including a hardener or catalyst configured to be mixed with the rapidly curable liquid gel prior to application of the rapidly curable liquid gel to the sampling surface.

[0007] In some embodiments, the polymer precursor mixture may include an acrylic resin that is polymerized on exposure to water vapor.

[0008] In some embodiments, the rapidly curable liquid gel may include a photoinitiator compound. In some embodiments, the photoinitiator compound may absorb UV light around 365 nm and/or 395 nm.

[0009] In some embodiments, the monomer may include a styrene derivative, an N-

Non-provisional patent application filed October 16th, 2017.